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(54) Title: LIGHT SENSITIVE MATERIALS FOR LITHOGRAPHIC PLATES

(57) Abstract

A method of producing a dye-containing positive working light sensitive material comprising reacting together a phenol or substituted phenol, formaldehyde and a dye capable of co-condensing with the formaldehyde and phenol or substituted phenol and then reacting the product with a quinone diazide. The material can be used as a coating for a lithographic printing plate, and can be applied directly to plates which have been anodised using sulphuric acid, without absorption of dye into the plate.

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LIGHT SENSITIVE MATERIALS FOR LITHOGRAPHIC PLATES

The invention relates to positive working light sensitive materials which can be used in the production of lithographic printing plates.

Light sensitive lithographic plates are produced by applying a light sensitive coating to a suitable support for example a plate of anodised aluminium. When the plate is exposed by light reaction in the coating results in the image areas having a different solubility from the non-image areas. Development with a suitable solvent can then selectively dissolve away the more soluble of the areas. A positive working plate is one in which the exposed, light-struck, areas are more soluble than the unexposed areas.

One system which is frequently used to provide a positive working light-sensitive material is a mixture of a quinone diazide with a novolak resin. On exposure light converts the quinone diazide to an indene carboxylic acid which is soluble in and developable by an alkaline aqueous developer of about pH 11.

Dyes are often included in the light sensitive materials so that the image can be visibly inspected. The dyes used are of two kinds, those which retain the same colour throughout the exposure and development process and those which change colour when exposed. In the case of the former the image is distinguished from the non-image when dye is selectively removed during development. In the latter case a change in colour occurs on irradiation so that the non-image area is distinguished from the image area. The colour change results from the use of a pH-indicating dye which, in the case where a quinone diazide is used as the light sensitive material, changes colour due to

increased acidity caused as the diazide converts to carboxylic acid groups. For example GB 1347759 describes a positive working material which exhibits a colour change upon exposure to light and which comprises in admixture a diazonium salt, a novolak resin and a hydroxy substituted aryl azo compound which undergoes a colour change in the presence of the acid produced by the diazonium salt on exposure to light.

Often the coating on a positive working lithoplate will be formulated to contain both a permanent dye and a pH indicating dye. In this way there is both a constant colour to the coating and a colour change on exposure.

Dye containing systems suffer from the drawback that they are not generally suitable for use directly on a freshly sulphuric acid anodised substrate. This is because the dye is absorbed by the substrate and can not be washed off during development. It is necessary for the plate to undergo a post anodic treatment before the coating of light sensitive material and dye is applied so as to pacify the substrate and prevent absorption of the dye on it. Various different post anodic treatments are commonly employed in the industry to achieve this, for example silicating, phosphating and treatment with polycarboxylic acid. These treatments have the effect of sealing the surface of the plate to prevent absorption of dye. Unfortunately the use of a post anodic treatment has the effect of reducing the press durability (run length) of a plate and also involves additional cost because of the extra manufacturing step involved.

There is thus a need for dye-containing positive working light sensitive materials for use as coatings for lithographic plates which can be applied directly

to freshly sulphuric acid anodised plates without absorption of dye into the plate.

In accordance with a first embodiment of the invention there is provided a method of producing a dye-containing positive working light sensitive material comprising reacting a novolak resin with a dye capable of reacting with phenolic -OH groups on the novolak and a quinone-diazide.

In accordance with a second embodiment of the invention there is provided a method of producing a dye-containing positive working light sensitive material comprising reacting together a phenol or substituted phenol, a reactive dye and formaldehyde and then reacting the product with a quinone diazide.

The present invention thus provides two methods of producing light sensitive materials in which a dye is incorporated directly in the molecule of light sensitive novolak rather than being present as a separate component in a light sensitive composition.

When light sensitive materials produced according to either of these methods are used as coatings directly on freshly sulphuric acid anodised lithographic plates and subsequently irradiated and developed the background (non-image) areas are not dye stained. It is thought that the extra bulk and large molecular weight of the dye which is bound to the novolak prevents it from being absorbed.

In the first embodiment the dye-containing novolak is prepared by reacting a pre-prepared novolak resin with both a dye and a quinone diazide. For the necessary reaction to occur the dye must be one which is capable of reacting with phenolic -OH groups on the novolak. The quinone diazide reacts with other phenolic -OH groups on the novolak. The dye may be a permanent dye or a pH-indicating dye provided it can undergo the necessary reaction.

Examples of dyes which have been found to work particularly well in this first method are permanent dyes such as those which contain a cyanuric chloride or sulphonyl chloride group. Specific examples are the commercially available Procion dyes such as Procion blue MX-G available from ICI.

Novolak resins which may be employed in this embodiment include those commonly used to prepare positive working light sensitive materials. Such novolaks are formed by condensing phenol or substituted phenol with formaldehyde. Specific examples of such novolaks include those based on cresol formaldehyde, such as Bakelite.

In the second embodiment the dye-containing light sensitive material is prepared by reacting a dye into the polymer chain at the same time as the novolak is formed by reaction of a phenol or substituted phenol with formaldehyde. In this case the dye reacts into the molecule in a different way by co-condensing with the formaldehyde and phenol or substituted phenol. The co-condensed polymer is then reacted with a quinone diazide which reacts with phenolic -OHs of the polymer.

This embodiment may be used to produce light sensitive materials containing either permanent or pH indicating dyes. Thus, the permanent dyes mentioned above may be used. It is, however, particularly suitable for use with pH indicating dyes, for example phthaleins or sulphophthaleins. A particular example of a sulphophthalein dye which may be employed in this embodiment is Phenol Red.

Phenol or substituted phenol compounds which may be employed in this embodiment include those commonly used to produce novolak resins.

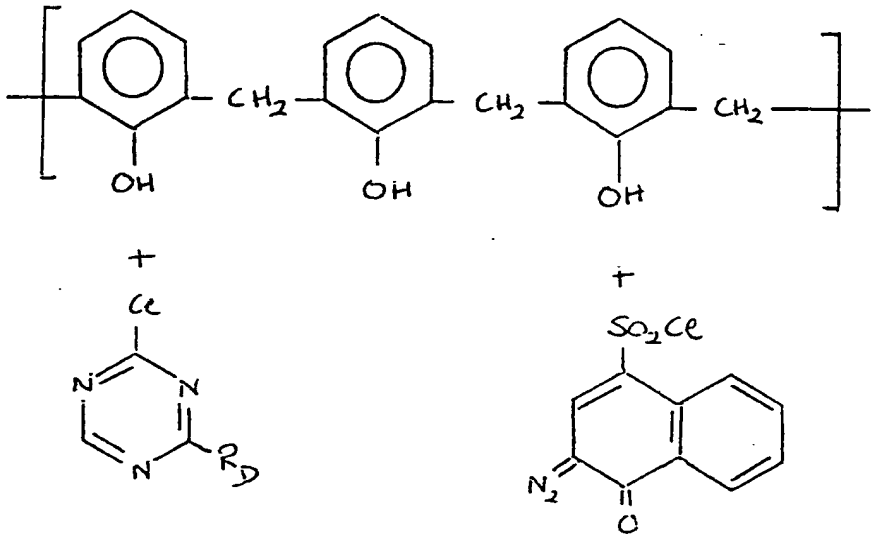
The quinone diazide used as the light sensitive component of the material includes those

conventionally employed in light sensitive coatings for lithoplates, for example a napthaquinone diazide sulphonyl chloride. Specific examples include 2-diazo-1-naphthol-4-sulphonyl chloride and 2-diazo-1-naphthol-5-sulphonyl chloride.

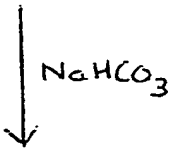
The present invention includes positive working light sensitive material produced by the methods of the first and second embodiments of the invention. In general the invention consists of positive working light sensitive material comprising a novolak resin which is functionalised with both a dye and a quinone diazide.

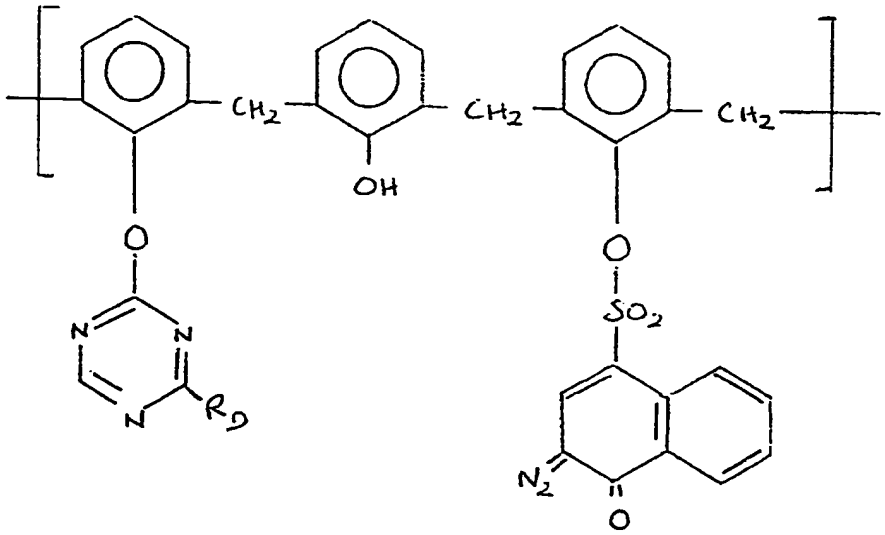
The reaction schemes involved in the production of the positive working light sensitive materials by the methods of the first and second embodiments of the invention are illustrated below.

REACTION SCHEME - ROUTE 1

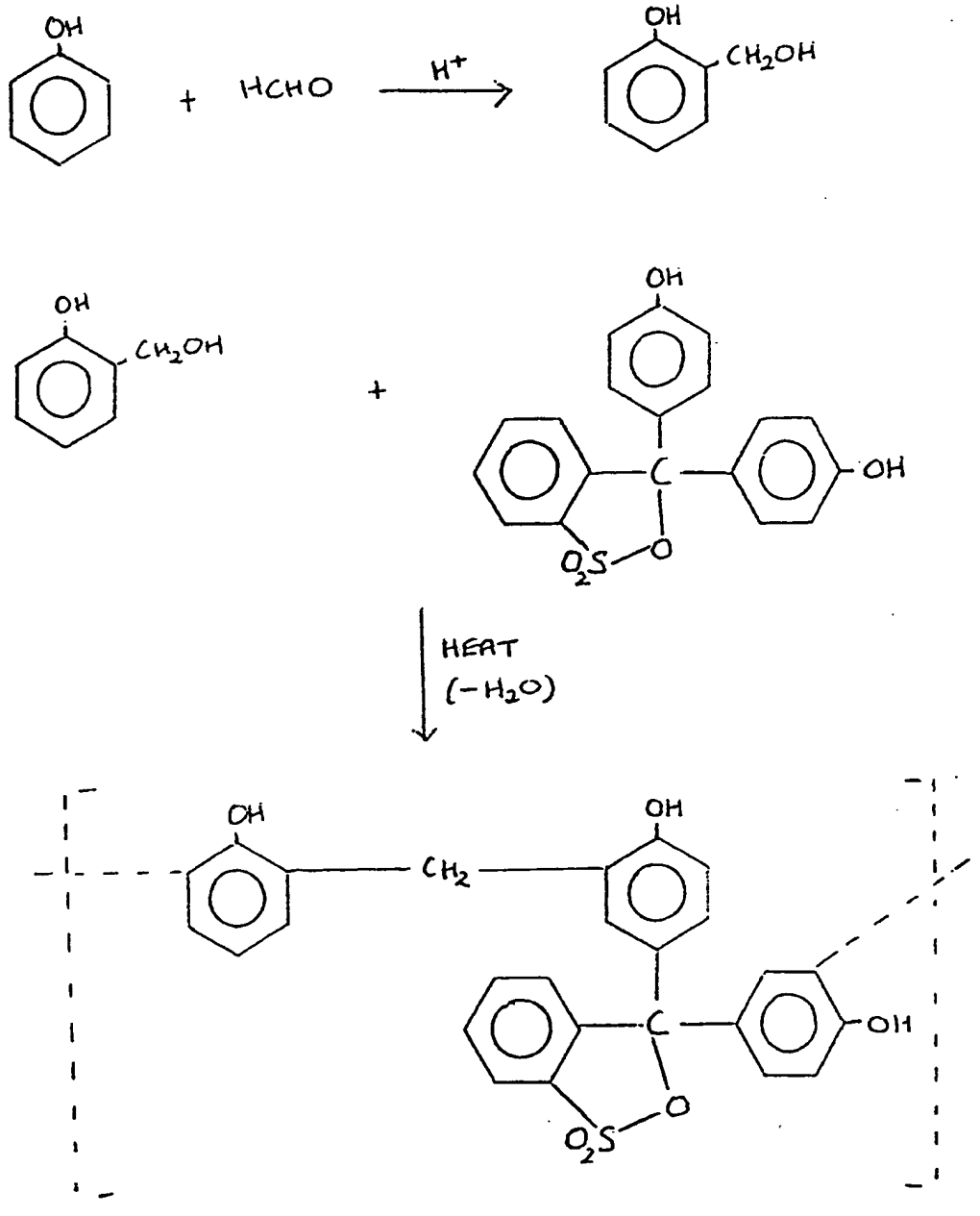


where R_D = a dye





REACTION SCHEME - ROUTE 2



The invention is illustrated by the following examples.

Example 1

Production of a positive working light sensitive material by reaction of a novolak resin with a dye and a napthaquinone-diazide sulphonyl chloride.

5.00g of Bakelite LB744, a novolac resin based on cresol formaldehyde, was dissolved in 16g of 2-methoxy ethanol with stirring. To this mixture was added 0.82g of sodium hydrogen carbonate, 5.00g water, 0.85g Procion blue MX-G (available from ICI) and 1.32g of 2-diazo-1-napthol-4-sulphonyl chloride (DNSC). This reaction mixture was stirred for two hours at 20°C during which the Procion blue dye reacted with some of the phenolic -OH groups of the novolak while the DNSC reacted with some of the other available phenolic -OH groups, to produce a resin functionalised with both dye and the photosensitising napthoquinone diazide. The mildly alkali sodium hydrogen carbonate was present to counter the acid HCl produced during the reaction. Product was recovered by precipitation into acidified water, followed by filtration, washing and drying.

The light sensitive product obtained was then used to produce a positive working lithographic plate. The product was dissolved in 2-methoxy ethanol at a concentration of 20% w/w and then coated onto an aluminium sheet which had been freshly anodised with sulphuric acid. After drying the coated sheet was exposed with UV radiation. This caused a reaction in the light sensitive napthoquinone diazide functional groups of the exposed background areas which rendered

them more soluble than the image areas. Thus, subsequent development in aqueous alkaline solution selectively dissolved away the background to reveal a coloured image. There was no dye staining of the background (non-image areas).

The Procion blue provides a permanent dye colour which does not change exposure.

Example 2

Production of a polymeric dye by a co-condensation reaction of a phenolic compound and a dye with formaldehyde.

37.6g of Phenol Red, 68.0g of phenol, 56.7g of formaldehyde (37% aqueous solution), 20.0g of water and 3.0g of oxalic acid were mixed together and the mixture refluxed for three hours. The water was then removed under vacuum until a sample formed a brittle solid on cooling.

In order to obtain a pH indicator operating in a most suitable range (pH 2.5 to 5.0) bromination of the phenol/Phenol Red/formaldehyde condensate obtained above was carried out as follows.

To 10g of the product obtained above in 100g of sodium hydroxide there was added a solution of bromine in aqueous solution bromide until a dark red solid separated which was filtered off and dried.

A coatable composition was prepared from the following ingredients:

Bakelite LB744/naphthoquinone diazide sulphonate	16% w/v
Brominated phenol/Phenol Red/ formaldehyde condensate	4% w/v
2-methoxy ethanol	80% w/v

The composition was bar coated onto a freshly sulphuric acid anodised sheet of aluminium and imagewise exposed to active radiation. The composition showed a distinct colour change from blue to yellow. The plate was then developed in an aqueous alkaline solution which removed the yellow exposed non-image areas of the coating to reveal the anodic film which showed no staining.

CLAIMS:

1. A method of producing a dye-containing positive working light sensitive material comprising reacting a novolak resin with a dye capable of reacting with phenolic -OH groups on the novolak and a quinone diazide.

2. A method of producing a dye-containing positive working light sensitive material comprising reacting together a phenol or substituted phenol, formaldehyde and a dye capable of co-condensing with the formaldehyde and phenol or substituted phenol and then reacting the product with a quinone diazide.

3. A method as claimed in claim 2 in which the dye is a pH-indicating dye.

4. A method as claimed in claim 3 in which the dye is a phthalein or sulphophthalein dye.

5. A method as claimed in claim 4 in which the dye is Phenol Red.

6. A method as claimed in claim 1 or claim 2 in which the dye is a permanent dye.

7. A method as claimed in claim 6 in which the dye contains a cyanuric chloride or sulphonyl chloride group.

8. A method as claimed in claim 7 in which the dye is a Procion dye.

9. A method as claimed in any one of claims 1 to 8

in which the quinone diazide is a napthaquinone diazide sulphonyl chloride.

10. A method as claimed in claim 9 in which the quinone diazide is 2-diazo-1-naphthol-4-sulphonyl chloride or 2-diazo-1-naphthol-5-sulphonyl chloride.

11. A positive working light sensitive material produced by the method of any one of claims 1 to 10.

12. A positive working light sensitive material comprising a novolak resin which is functionalised with both a dye and a quinone diazide.

13. A material as claimed in claim 12 in which the quinone diazide functionality has been provided by reaction with napthaquinone diazide sulphonyl chloride.

14. A material as claimed in claim 13 in which the quinone diazide functionality has been provided by reaction with 2-diazo-1-naphthol-4-sulphonyl chloride or 2-diazo-1-naphthol-5-sulphonyl chloride.

15. A material as claimed in any one of claims 12 to 14 in which the dye functionality is pH-indicating.

16. A material as claimed in claim 15 in which the dye functionality has been provided by reaction with a phthalein or sulphophthalein dye.

17. A material as claimed in claim 16 in which the dye functionality has been provided by reaction with Phenol Red.

18. A material as claimed in any one of claims 12 to

14 in which the dye functionality comprises a permanent dye.

19. A material as claimed in claim 18 in which the dye functionality has been provided by reaction with a dye containing a cyanuric chloride or sulphonyl chloride group.

20. A material as claimed in claim 19 in which the dye functionality has been provided by reaction with a Procion dye.

INTERNATIONAL SEARCH REPORT

International Appl[redacted] No PCT/GB 91/00858

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 G03F7/023 ; G03F7/105

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	G03F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X,Y	DATABASE WPI, no. 71-70002s Derwent Publications Ltd, London, GB & SU-A-289389 (Bokov y. et al.) * The whole abstract * ---	2-5, 11, 15-17
Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 172 (P-862)(3520) 24 April 1989, & JP-A-01 006946 (KONIKA CORP) 11 January 1989, see the whole document ---	2-5, 11, 15-17
A	US,A,3929488 (SMITH P.J.) 30 December 1975 see the whole document & GB,A,1347759 (cited in the application) ---	

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
20 AUGUST 1991	[illegible]
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	LUDI M.M.B.

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 9100858
SA 47973

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-3929488	30-12-75	AT-B-	320685	25-02-75
		AU-B-	457866	24-01-75
		AU-A-	4349372	20-12-73
		CA-A-	970203	01-07-75
		CH-A-	542460	15-11-73
		DE-A,C	2229365	21-12-72
		FR-A,B	2147938	11-03-73
		GB-A-	1347759	27-02-74
		NL-A-	7208251	19-12-72
		BE-A-	784985	16-10-72
		SE-B-	380636	10-11-75